

Rigorous Treatment of the Van Der Waals-Maxwell Theory of the Liquid-Vapor Transition*

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Rigorous upper and lower bounds are obtained for the thermodynamic free-energy density $a(\rho, \gamma)$ of a classical system of particles with two-body interaction potential $g(r) + \gamma\varphi(\gamma r)$ where ν is the number of space dimensions and ρ the density, in terms of the free-energy density $a^0(\rho)$ for the corresponding system with $\varphi(\mathbf{x}) = 0$. When $\varphi(\mathbf{x})$ belongs to a class of functions, which includes those which are nonpositive and those whose ν -dimensional Fourier transforms are nonnegative, the upper and lower bounds coincide in the limit $\gamma \rightarrow 0$ and $\lim_{\gamma \rightarrow 0} a(\rho, \gamma)$ is the maximal convex function of ρ not exceeding $a^0(\rho) + \frac{1}{2}\alpha\rho^2$, where $\alpha = \int \varphi(\mathbf{x}) d\mathbf{x}$. The corresponding equation of state is given by Maxwell's equal-area rule applied to the function $p^0(\rho) + \frac{1}{2}\alpha\rho^2$ where $p^0(\rho)$ is the pressure for $\varphi(\mathbf{x}) = 0$. If $a^0(\rho) + \frac{1}{2}\alpha\rho^2$ is not convex the behavior of the limiting free energy indicates a first-order phase transition. These results are easily generalized to lattice gases and thus apply also to Ising spin systems.

The two-body distribution function is found, in the limit $\gamma \rightarrow 0$, to be normally identical with that for $\varphi(\mathbf{x}) = 0$, but if the system has a phase transition it has the form appropriate to a two-phase system.

Some of the upper and lower bounds on $a(\rho, \gamma)$ are simple enough to be useful for finite γ . Also, some of our results remain valid for quantum systems.

I. INTRODUCTION

PHASE transitions such as melting and boiling are familiar experiences, but their explanation from the first principles of statistical mechanics still presents a major challenge to the theoretical physicist. One of the earliest steps towards a theory of the gas-liquid phase transition was taken by van der Waals.¹ Seeing the interaction between the molecules of a classical fluid as a competition between two distinct parts of the intermolecular force, a short-range repulsive part and a long-range attractive part, he arrived at the equation of state

$$p = kT\rho/(1 - \rho b) + \frac{1}{2}\alpha\rho^2 \equiv p_{dw}(\rho, T) \quad (1.1)$$

where p is the pressure, k Boltzmann's constant, T the temperature, ρ the number density, and $-\alpha$ and b are positive constants characterizing long- and short-range parts of the potential, respectively.

When T exceeds the critical temperature $T_c \equiv -4\alpha/27bk$, the van der Waals equation of state (1) gives a good qualitative representation of the isotherms of a real fluid; for $T < T_c$, however, each isotherm includes a section where the compressibility is negative, in violation of the thermodynamic stability principle. The reason for this failure is that the argument leading to (1) assumes a single-phase system; it does not allow for the possibility of coexisting liquid and vapor phases.

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¹ J. van der Waals, thesis (Leiden, 1873) (cited by Kac, Uhlenbeck, and Hemmer, Ref. 6 of this paper).

Maxwell² showed that the coexistence region could be included in the theory by using van der Waals' equation of state for both liquid and vapor phases and using the thermodynamic equilibrium condition that the two phases must have equal pressures and chemical potentials. This leads to the following modification of (1) for $T < T_c$:

$$p = \begin{cases} p_{dw}(\rho, T) & \text{if } \rho < \rho_s(T) \text{ or } \rho > \rho_l(T) \\ p_{sat}(T) & \text{if } \rho_s(T) < \rho < \rho_l(T) \end{cases} \quad (1.2)$$

where $\rho_s(T)$, $\rho_l(T)$ and $p_{sat}(T)$ may be determined by the graphical construction shown in Fig. 1.

A very interesting derivation of van der Waals' equation of state with Maxwell's rule was given recently by van Kampen.³ In this derivation the volume Ω occupied by the system is divided into a large number of cells, each small compared with the range of the long-range attractive force, but large enough to contain many particles. Avoiding the pitfall of assuming a uniform distribution of particles over cells, which leads⁴ to a generalized form of the van der Waals equation of state, van Kampen obtained the distribution over cells by minimizing the free energy. His method leads to the modified equation of state (2), which implies a first-order phase transition. When $\rho < \rho_s$ or $\rho_l < \rho$, van Kampen's method indeed gives a uniform distribution over cells, but when $\rho_s < \rho < \rho_l$ it leads

² J. C. Maxwell, Scientific Papers (Dover Reprint, New York), p. 425.

³ N. G. van Kampen, Phys. Rev. **135**, A362 (1964).

⁴ O. Ornstein, thesis (Leiden, 1908) (cited by N. G. van Kampen, Ref. 3 of this paper).

to the conclusion that this distribution is nonuniform, as it should be when two phases coexist.

Van Kampen's treatment is, however, not mathematically rigorous. In particular the conditions to be satisfied by the interaction are not specified, and various limiting processes are hinted at but not carried out explicitly. It is the purpose of the present paper to provide a rigorous treatment similar to van Kampen's and to extend it to a more general class of long-range potentials than the purely attractive potentials considered by van Kampen.

The intermolecular potential we consider has the form proposed by Kac⁵ and investigated thoroughly for a one-dimensional system by Kac, Uhlenbeck, and Hemmer,⁶

$$v(r) = q(r) + w(r, \gamma), \quad (1.3)$$

where r represents the separation of a pair of particles, $q(r)$ is a short-range potential, and $w(r, \gamma)$ is a potential (we call it the *Kac potential*) whose range is proportional to the reciprocal of the parameter γ . Kac, Uhlenbeck, and Hemmer studied a one-dimensional system with

$$q(r) \equiv \begin{cases} +\infty & \text{if } r < r_0, \\ 0 & \text{if } r > r_0, \end{cases} \quad (1.4)$$

$$w(r, \gamma) \equiv \frac{1}{2}\alpha\gamma \exp(-\gamma r), \quad (1.5)$$

where r_0 , γ , and $-\alpha$ are positive parameters. For finite γ they found no phase transition, but in the *van der Waals limit* $\gamma \rightarrow 0$ the equation of state approaches as a limit Maxwell's modification (2) of the van der Waals equation of state and thus does show a first-order phase transition. Unfortunately their method is very difficult to generalize to other potentials or to more than one dimension.

An important feature of the work of Kac, Uhlenbeck, and Hemmer was the use of the limit process $\gamma \rightarrow 0$ to provide a clear distinction between the short (finite) range of the contribution $q(r)$ to $v(r)$ and the long (infinite as $\gamma \rightarrow 0$) range of the contribution $w(r, \gamma)$. It is this feature which we shall exploit here; but unlike Kac, Uhlenbeck, and Hemmer, we do not restrict the system to one dimension nor the potential to the form defined by (4) and (5). Instead of the special form (5) for $w(r, \gamma)$, we use

$$w(r, \gamma) = \gamma^\nu \varphi(\gamma r), \quad (1.6)$$

where ν is the number of dimensions of the space

⁵ M. Kac, *Phys. Fluids* **2**, 8 (1959).

⁶ M. Kac, G. E. Uhlenbeck, and P. Hemmer, *J. Math. Phys.* **4**, 216 (1963).

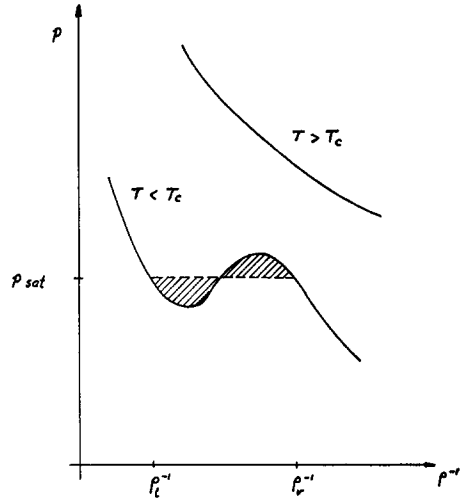


FIG. 1. Typical isotherms for the van der Waals equation of state (solid lines) and Maxwell's modification (dotted line). The shaded areas are equal.

considered; this reduces to (5) if $\nu = 1$ and $\varphi(x) = \frac{1}{2}\alpha e^{-x}$. If the function $\varphi(x)$ is bounded in a neighborhood of the origin, say in $x < \delta$, then the Kac potential (6) has the property

$$|w(r, \gamma)| < \gamma^\nu \text{Max}_{x < \delta} |\varphi(x)| \quad \text{if } \gamma < \delta/r \quad (1.7)$$

so that

$$\lim_{\gamma \rightarrow 0} w(r, \gamma) = 0 \quad \text{for all } r. \quad (1.8)$$

At the same time the integral of the Kac potential over all ν -dimensional space,

$$\int w(r, \gamma) dr = \int \varphi(x) dx \equiv \alpha, \quad (1.9)$$

is independent of γ . This fact is compatible with (1.8) because the limit operation $\gamma \rightarrow 0$ does not commute with the one associated with the infinite region of integration.

The basis of our method is to obtain upper and lower bounds on the free energy

$$A(N, \Omega, \gamma) \equiv -kT \log Z(N, \Omega, \gamma), \quad (1.10)$$

where $Z(N, \Omega, \gamma)$ is the classical partition function for N particles at temperature $T \equiv 1/k\beta$ in a ν -dimensional cube Ω , defined by

$$Z(N, \Omega, \gamma) \equiv (1/N!)(mkT/2\pi\hbar^2)^{\nu N/2} \times \int_{\Omega} \cdots \int_{\Omega} e^{-\beta V} d\mathbf{x}_1 \cdots d\mathbf{x}_N \quad (1.11)$$

and

$$V \equiv \sum_{i \leq j \leq N} v(\mathbf{x}_i - \mathbf{x}_j) \quad (1.12)$$

with $v(\mathbf{r})$ defined in (3). The upper and lower bounds are obtained by dividing the cube Ω into M congruent smaller cubes $\omega_1 \cdots \omega_M$ and using estimates of the interactions across cell boundaries to relate the free energy of the cube Ω to the sum of the free energies of the cubes $\omega_1 \cdots \omega_M$.

From these upper and lower bounds, the equation of state in the van der Waals limit is calculated by means of a succession of limit operations. First the thermodynamic free energy is calculated from $A(N, \Omega, \gamma)$ by taking the *thermodynamic limit*. The simplest way of taking this limit is to double the side of the cube Ω repeatedly, adjusting N at each step to the value $\rho\Omega$ where ρ , the density, is a constant, and the symbol Ω is used to represent the volume of the cube as well as the cube itself. The thermodynamic free-energy density, a function of ρ and γ , is then defined as

$$a(\rho, \gamma) \equiv \lim_{\Omega \rightarrow \infty} A(\rho\Omega, \Omega, \gamma)/\Omega \quad (1.13)$$

where $A(N, \Omega, \gamma)$ may be defined for nonintegral N by linear interpolation.⁷

The next operation is to take the van der Waals limit $\gamma \rightarrow 0$. This gives the *van der Waals free-energy density*

$$\begin{aligned} a(\rho, 0+) &\equiv \lim_{\gamma \rightarrow 0} a(\rho, \gamma) \\ &= \lim_{\gamma \rightarrow 0} \lim_{\Omega \rightarrow \infty} A(\rho\Omega, \Omega, \gamma)/\Omega. \end{aligned} \quad (1.14)$$

It is important to take these two limits in the right order. Taking the limit $\Omega \rightarrow \infty$ first, as in (14), means that the range of the Kac potential, although very large, is much less than the size of the container. If they are taken in the opposite order, then the Kac potential has a range much larger than the size of the container and in consequence of (8) its effect disappears. In fact, by applying (8) to (10) and (11) we obtain

$$\lim_{\gamma \rightarrow 0} A(N, \Omega, \gamma) = A^0(N, \Omega), \quad (1.15)$$

where A^0 is the free energy for N particles of the *reference system* in a cube Ω . By reference system we mean one for which the interaction potential is $q(\mathbf{r})$ instead of $q(\mathbf{r}) + w(\mathbf{r}, \gamma)$. Taking the thermodynamic limit of (15) we obtain, in contrast to (14), the formula

$$\lim_{\Omega \rightarrow \infty} \lim_{\gamma \rightarrow 0} A(\rho\Omega, \Omega, \gamma)/\Omega = a^0(\rho) \quad (1.16)$$

where

$$a^0(\rho) \equiv \lim_{\Omega \rightarrow \infty} A^0(\rho\Omega, \Omega)/\Omega \quad (1.17)$$

is the thermodynamic free-energy density of the reference system at particle density ρ , and is not in general equal to $a(\rho, 0+)$.

The upper and lower bounds on $A(N, \Omega, \gamma)$ which we shall derive lead to upper and lower bounds on $a(\rho, 0+)$. These bounds depend on the volume ω of the cells ω_i used. The bounds can be simplified by a third limit process $\omega \rightarrow \infty$, after which, in favorable cases, the upper and lower bounds are equal so that $a(\rho, 0+)$ can be calculated. This triple limit process corresponds to the following relationships:

$$r_0 \ll \omega^{1/3} \ll \gamma^{-1} \ll \Omega^{1/3} \quad (1.18)$$

among the four characteristic lengths of our calculation: the range of the short-range potential, the size of the cells, the range of the Kac potential, and the size of the container.

Once $a(\rho, 0+)$ has been found, the equation of state can be calculated by differentiation. The main result of our work is to show rigorously that under suitable conditions the equation of state is indeed given by Maxwell's rule (2) applied to the generalized van der Waals isotherm

$$\tilde{p}_{\text{adv}}(\rho, T) = p^0(\rho, T) + \frac{1}{2}\alpha\rho^2 \quad (1.19)$$

where $p^0(\rho, T)$ is the pressure of the reference system, calculated by differentiation from $a^0(\rho)$. This result can be used to investigate the conditions under which the system will have a first-order phase transition in the van der Waals limit. A further result is to show, by studying the two-particle distribution function, that if there is such a first-order phase transition then two phases of different densities are present during the transition.

For rigorous arguments it is necessary to impose conditions on the short- and long-range potentials. We shall assume that the short-range potential satisfies

$$q(\mathbf{r}) = +\infty \quad \text{for } r < r_0, \quad (1.20a)$$

$$|q(\mathbf{r})| < D_2 r^{-r-\epsilon} \quad \text{for } r_0 < r, \quad (1.20b)$$

where r_0 (the hard-core diameter), D_2 , and ϵ are positive constants; and we shall also assume that the shape function $\varphi(\mathbf{x})$ of the Kac potential satisfies

$$|\varphi(\mathbf{r})| < D_3 r^{-r-\epsilon} \quad \text{for all } r, \quad (1.21a)$$

$$\varphi(\mathbf{r}) \text{ is continuous at } r = 0, \quad (1.21b)$$

$$\int \varphi(\mathbf{r}) d\mathbf{r} \text{ exists as a Riemann integral.} \quad (1.21c)$$

Further, when in Sec. V the function $\varphi(\mathbf{r})$ is ex-

⁷ M. Fisher, Arch. Rat. Mech. Anal. 17, 377 (1964).

pressed as the sum of two parts satisfying the conditions (5.2), both parts are required to satisfy (1.21). The extent to which the conditions (1.20) and (1.21) can be weakened will be discussed in Sec. IX, along with the possibilities for generalizing this work to quantum systems and to lattice gases.

II. UPPER BOUND ON THE FREE ENERGY

Finding an upper bound on the free energy is equivalent to finding a lower bound on the partition function. To obtain a lower bound, we divide the cube Ω into M smaller cubical regions $\omega_1 \cdots \omega_M$, each of side $(s + t)$ where s and t are positive lengths such that $(s + t)$ is a submultiple of the side of Ω (see Fig. 2). Since the small cubes completely fill Ω its volume, which we also call Ω , is given by

$$\Omega = M(s + t)^3. \quad (2.1)$$

For each ω_i , let ω'_i be the cube of side s consisting of all points within ω_i whose distance from the boundary of ω_i is at least $\frac{1}{2}t$. A lower bound on $Z(N, \Omega, \gamma)$ can be obtained by selecting any set of integers $N_1, N_2, \cdots N_M$ which add up to N , and considering only the contribution to the integral in (1.11) from configurations where there are N_1 particles in the cell ω'_1 , N_2 in ω'_2 , and so on. The quantity so calculated we denote by $\tilde{Z}(N_1, N_2 \cdots N_M)$. There are $N!/(N_1!N_2! \cdots N_M!)$ ways of choosing the N_1 particles to go in the cell ω'_1 , N_2 to go in ω'_2 , etc., and since the particles are identical all these different ways give the same contribution to the integral. Multiplying a typical contribution by $N!/\prod N_i!$ we thus obtain

$$\begin{aligned} Z &\geq \tilde{Z}(N_1, N_2 \cdots N_M) \\ &= \prod_i [(1/N_i!)(m/2\pi\hbar^2\beta)^{N_i/2}] \\ &\quad \times \int_{\omega'_1} \cdots \int_{\omega'_M} e^{-\beta V} d\mathbf{x}_1 \cdots d\mathbf{x}_N, \end{aligned} \quad (2.2)$$

where the first N_1 of the N ν -fold integrations are taken over the region ω'_1 , the next N_2 over ω'_2 , and so on.

To obtain a lower bound on the integral in (2.2) we write

$$V = V' + V'' \quad (2.3)$$

where V' is the contribution to the total potential energy from pairs of particles that are both in the same cell, and V'' is the contribution from pairs that are in different cells. If $V''_{\max}$ is some upper bound on V'' , then (2) implies

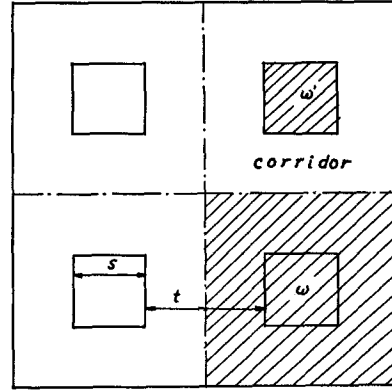


Fig. 2. Division of Ω into cells.

$$\begin{aligned} \tilde{Z} &\geq \prod_i [(1/N_i!)(m/2\pi\hbar^2\beta)^{N_i/2}] \\ &\quad \times \int_{\omega'_1} \cdots \int_{\omega'_M} e^{-\beta V' - \beta V''_{\max}} d\mathbf{x}_1 \cdots d\mathbf{x}_N \\ &= [\prod_i Z(N_i, \omega', \gamma)] e^{-\beta V''_{\max}}, \end{aligned} \quad (2.4)$$

where $Z(N_i, \omega', \gamma)$ is the partition function for N_i particles in a cube ω' , of side s .

To obtain a lower bound on the exponential factor in (4) we consider the short- and long-range contributions separately, writing

$$V'' = Q'' + W''. \quad (2.5)$$

A convenient upper bound for W'' , the long-range contribution to V'' , is

$$W'' \leq \sum_{i < j} N_i N_j w_{\max}(\mathbf{k}_{ij}) \quad (2.6)$$

where

$$\begin{aligned} w_{\max}(\mathbf{k}_{ij}) &= \text{Max}_{\substack{\mathbf{x} \in \omega_i \\ \mathbf{y} \in \omega_j}} w(\mathbf{x} - \mathbf{y}, \gamma) \\ &= \text{Max}_{\mathbf{r} \in \omega_0} w(\mathbf{k}_{ij} + 2\mathbf{r}, \gamma) \end{aligned} \quad (2.7)$$

where ω_0 is a cube of side $(s + t)$ centered at the origin, and $\mathbf{k}_{ij}$ is the vector from the center of ω_i to that of ω_j . For an upper bound on Q'' , the short-range contribution to V'' , we may use the same method, in conjunction with the condition (1.20), and obtain, if $t > r_0$, the upper bound

$$\begin{aligned} Q'' &\leq D_2 \sum_{i < j} N_i N_j (r_{ij, \min})^{-\nu-\epsilon} \\ &= \frac{1}{2} D_2 \sum_i N_i \sum'_j N_j (r_{ij, \min})^{-\nu-\epsilon}, \end{aligned} \quad (2.8)$$

where $r_{ij, \min}$ is the least distance from ω'_i to ω'_j and $\sum'_j$ means a sum with the $j = i$ term omitted. To estimate this last sum we may group the cubes ω'_i into shells centered on ω'_i . The first shell contains

$3' - 1$ cubes, all points of which are a distance at least t from all points of ω'_i , the next shell contains $5' - 3'$ cubes, each one at least $2t + s$ from ω'_i ; and so on. Writing also $N_{\max}$ for the maximum value of N_i , we obtain

$$\begin{aligned} Q'' &\leq \frac{1}{2} D_2 \sum_i N_i \sum_{n=1}^{\infty} N_{\max} [(2n+1)' \\ &\quad - (2n-1)'] / (nt + (n-1)s)^{r+\epsilon} \\ &\leq \frac{1}{2} D_2 N N_{\max} J, t^{-r-\epsilon} \end{aligned} \quad (2.9)$$

where

$$J, = \sum_{n=1}^{\infty} n^{-r-\epsilon} [(2n+1)' - (2n-1)'] < \infty. \quad (2.10)$$

Substituting (9) and (6) into (5), (4), and (2), we obtain

$$\begin{aligned} A(N, \Omega, \gamma) &\leq \sum_i A(N_i, \omega'_i, \gamma) \\ &\quad + \sum_{i < j} N_i N_j w_{\max}(\mathbf{k}_{ij}) + \frac{1}{2} D_2 J, N N_{\max} t^{-r-\epsilon}, \end{aligned} \quad (2.11)$$

where $A(N, \Omega, \gamma)$ is defined in (1.10). The upper bound (11) holds for any choice of $N_1, N_2, \dots, N_M$ whose sum is N , and in particular for the choice which minimizes the right side.

To obtain an upper bound on the thermodynamic free energy in the van der Waals limit, we apply the triple limit process described in Sec. 1 to the inequality (11). This is simplest for the case where all of $N_1, N_2, \dots, N_M$ are equal:

$$N_1 = N_2 = \dots = N_M = \rho(s+t)'. \quad (2.12)$$

Replacing $\sum_{i < j}$ in (2.11) by $\frac{1}{2} \sum_i \sum_j'$ and dividing both sides by Ω we obtain

$$\begin{aligned} A(\rho\Omega, \Omega, \gamma)/\Omega &\leq [M/\Omega] A(\rho(s+t)', \omega', \gamma) \\ &\quad + \frac{1}{2} [\rho^2(s+t)^{2r}/\Omega] \sum_i \sum_j' w_{\max}(\mathbf{k}_{ij}) \\ &\quad + \frac{1}{2} D_2 J, \rho^2(s+t)' t^{-r-\epsilon}. \end{aligned} \quad (2.13)$$

To take the limit $\Omega \rightarrow \infty$ we require the following lemma:

$$\lim_{\Omega \rightarrow \infty} 1/M \sum_i \sum_j' w_{\max}(\mathbf{k}_{ij}) = \sum_{\mathbf{k}}' w_{\max}(\mathbf{k}) \quad (2.14)$$

where $\sum_{\mathbf{k}}'$ is an infinite sum over the complete infinite lattice of possible vectors $\mathbf{k}_{ij}$, except $\mathbf{k} = 0$. To prove (14) it is sufficient to show that the difference between its two sides vanishes. This difference can be written as the limiting value, for large M , of the expression

$$1/M \sum_i \sum_j'' w_{\max}(\mathbf{k}_{ij}) \quad (2.15)$$

with $\sum_j''$ meaning the sum over an infinite network of cells outside Ω , continuing the pattern established by the cells inside Ω , but not including the cells inside Ω . Let δ be any small positive number. By (1.6) and (1.21a), the infinite sum on the right of (14) converges absolutely, and therefore we can find a number σ such that

$$\sum_{|\mathbf{k}| > \sigma}' |w_{\max}(\mathbf{k})| < \frac{1}{2} \delta. \quad (2.16)$$

The sum over i in (15) may be divided into two parts, the first part including all those cells whose distance from the boundary of Ω is greater than σ , and the second, those for which it is not. For each value of i in the first part of the i -summation, the sum over j covers only a subset of the values of k covered in the sum (15), and hence this part of the i -summation contributes at most $\frac{1}{2} \delta$ to the expression (16). In the second part of the i -summation, the number of terms is at most $[\Omega - (\Omega^{1/r} - 2\sigma)^r]/(s+t)'$, and this number does not exceed $2\nu\sigma \Omega^{1-1/r}(s+t)'^{-\nu}$ because

$$x^r - y^r \leq r x^{r-1}(x-y) \quad \text{if } x \geq y \geq 0. \quad (2.17)$$

Consequently, by (1), the second part of the i -summation contributes to the expression (15) an amount not exceeding $2\nu\sigma \Omega^{-1/r} \sum_j' |w_{\max}(\mathbf{k})|$, which can be made $< \frac{1}{2} \delta$ by making Ω large enough. Thus the complete expression (15) is less than δ for all large Ω , and since δ is arbitrarily small, the result (14) follows from the definition of a limit, Q.E.D.

Taking the thermodynamic limit of (13) with the help of (1) and (14) we obtain

$$\begin{aligned} a(\rho, \gamma) &\leq A(\rho(s+t)', \omega', \gamma)/(s+t)' \\ &\quad + \frac{1}{2} \rho^2(s+t)' \sum_{\mathbf{k}}' w_{\max}(\mathbf{k}) \\ &\quad + \frac{1}{2} D_2 J, \rho^2(s+t)' t^{-r-\epsilon}. \end{aligned} \quad (2.18)$$

The second limiting process is the van der Waals limit $\gamma \rightarrow 0$. To evaluate the van der Waals limit of the middle term on the right in (18) we substitute from (7) and (1.6), obtaining

$$(s+t)' \sum_{\mathbf{k}}' w_{\max}(\mathbf{k}) = 2^{-r} \sum_{\mathbf{n}}' \Delta \text{Max}_{\mathbf{x} \in \Delta_{\mathbf{n}}} \varphi(\mathbf{x}) \quad (2.19)$$

where the sum goes over all nonzero vectors $\mathbf{n}$ with integer components. $\Delta_{\mathbf{n}}$ stands for the cube of side $2\gamma(s+t)$ centered at the point $\gamma(s+t)\mathbf{n}$ with its sides parallel to those of Ω , and $\Delta \equiv 2^{-r}\gamma^r(s+t)'$ is the volume of one of the cubes $\Delta_{\mathbf{n}}$. The network of overlapping cubes $\Delta_{\mathbf{n}}$ can be disentangled into 2^r separate nonoverlapping networks, each of them just filling ν -dimensional space (except for one net-

work where the cube centered on the origin is missing). In the limit $\gamma \rightarrow 0$ these networks become infinitesimally fine and, by Riemann's definition of an integral,⁸ the contribution of each of them to the second sum in (19) tends to $\int \varphi(\mathbf{x}) d\mathbf{x}$; the van der Waals limit of (2.19) is therefore

$$(s+t)^\gamma \lim_{\gamma \rightarrow 0} \sum_{\mathbf{k}}' w_{\max}(\mathbf{k}) = \int \varphi(\mathbf{x}) d\mathbf{x} \equiv \alpha. \quad (2.20)$$

Using this result, and also (1.15), in (18) we obtain

$$a(\rho, 0+) \leq A^0(\rho(s+t)^\gamma, \omega')/(s+t)^\gamma + \frac{1}{2}\rho^2\alpha + \frac{1}{2}D_2J_\rho(s+t)^\gamma/t'^{++}. \quad (2.21)$$

The final limiting process is to make the cell size infinite by making $s \rightarrow \infty$. As Fisher has shown⁷ the last term in (21), which represents the short-range interactions between cells, can be eliminated if we make t depend on s in such a way that

$$t/s \rightarrow 0 \quad \text{and} \quad s'/t'^{++} \rightarrow 0 \quad \text{as} \quad s \rightarrow \infty. \quad (2.22)$$

This can be done, for example, by making $t \propto s^\eta$ where η is a constant satisfying

$$\nu/(\nu + \epsilon) < \eta < 1. \quad (2.23)$$

Applying this limit on both sides of (21) and using the continuity of $a^0(\rho)$, we obtain, since the volume of the cell ω' is s^ν ,

$$a(\rho, 0+) \leq a^0(\rho) + \frac{1}{2}\rho^2\alpha. \quad (2.24)$$

That is, in the van der Waals limit the increase in free-energy density brought about by introducing a Kac potential into a system with short-range forces cannot exceed the increase that one would calculate by treating the particles as a smoothed-out uniform medium.

The result (2.24) can be strengthened in some cases by using the fact^{7,9} that $a(\rho, \gamma)$ is a convex function¹⁰ of ρ , so that $a(\rho, 0+)$, being the limit of a sequence of convex functions, is also convex. Because of this (2.24) implies

$$a(\rho, 0+) \leq \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\} \quad (2.25)$$

where $\text{CE} \{f(\rho)\}$ means, for any function $f(\rho)$, the *convex envelope* of that function, defined as the maximal convex function not exceeding f :

$$\text{CE} \{f(\rho)\} \equiv \text{Max } \phi(\rho) \quad \text{for each value of } \rho$$

$$\left\{ \begin{array}{l} \phi(\cdot) \\ \phi(\cdot) \text{ is convex} \\ \phi(\xi) \leq f(\xi) \text{ for all } \xi \end{array} \right\}. \quad (2.26)$$

Since the maximum of any family of convex functions is¹¹ itself convex, the function $\text{CE} \{f(\rho)\}$ is convex. If $f(\rho)$ is convex, then $\text{CE} \{f(\rho)\}$ and $f(\rho)$ coincide; otherwise the graph of $\text{CE} \{f(\rho)\}$ consists partly of convex segments of the graph of $f(\rho)$ and partly of segments of double tangents of this graph (Fig. 3). The construction of $\text{CE} \{f(\rho)\}$ from $f(\rho)$ is sometimes called the *double tangent construction*.

It will be shown in Sec. VI that the replacement of $a^0(\rho) + \frac{1}{2}\alpha\rho^2$ by its convex envelope is equivalent to the replacement of van der Waals' equation of state by Maxwell's modification (1.2).

III. LOWER BOUNDS ON THE FREE ENERGY: NONNEGATIVE-DEFINITE KAC POTENTIALS

A lower bound on the free energy is most easily found when the shape function $\varphi(\mathbf{x})$ defining the Kac potential (1.6) is *nonnegative definite*: that is to say, when its ν -dimensional Fourier transform

$$\Phi(\mathbf{p}) \equiv \int \varphi(\mathbf{x}) \exp(2\pi i \mathbf{p} \cdot \mathbf{x}) d\mathbf{x} \quad (3.1)$$

is nonnegative. In this case it is possible to find a lower bound $W_{\min}$ on the long-range contribution

$$\begin{aligned} W &\equiv \sum_{i < j} \gamma' \varphi[\gamma(\mathbf{x}_i - \mathbf{x}_j)] \\ &= \frac{1}{2} \sum_i \sum_j \gamma' \varphi[\gamma(\mathbf{x}_i - \mathbf{x}_j)] - \frac{1}{2} N \gamma' \varphi(0) \end{aligned} \quad (3.2)$$

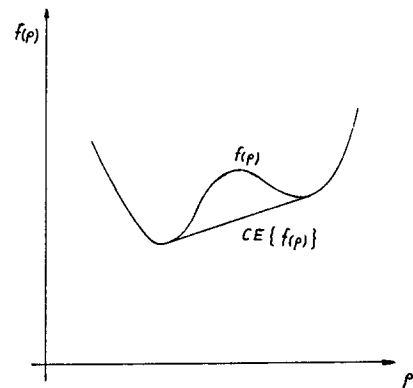


FIG. 3. A function $f(\rho)$ and its convex envelope.

⁸ W. Rogosinski, *Volume and Integral* (Oliver and Boyd, London, 1952), Theorem 58.

⁹ D. Ruelle, *Helv. Phys. Acta* **36**, 183 (1963).

¹⁰ G. Hardy, J. E. Littlewood, and G. Polya, *Inequalities* (Cambridge University Press, London and New York, 1959), Chap. 3.

¹¹ Proof: Since $\text{CE}\{f(\rho)\} \geq \phi(\rho)$ both ends of any chord of the graph $\text{CE}\{f(\rho)\}$ lie above or on the ends of the corresponding (same end ordinates) chord of any $\phi(\rho)$ and hence above or on the graph of $\phi(\rho)$ itself; consequently the chord of $\text{CE}\{f(\rho)\}$ also lies above or on the curve $\text{Max } \phi(\rho) \equiv \text{CE}\{f(\rho)\}$.

to the total potential energy V , and by substituting such a lower bound into the basic definitions (1.10) and (1.11) we obtain

$$A(N, \Omega, \gamma) \geq A^0(N, \Omega) + W_{\min}. \quad (3.3)$$

To find a suitable $W_{\min}$ we substitute the Fourier inversion formula of (1) into (2), obtaining

$$W = -\frac{1}{2}N\gamma'\varphi(0) + \frac{1}{2}\gamma' \int d\mathbf{p} \Phi(\mathbf{p}) \left| \sum_{i=1}^N \exp(2\pi i\gamma\mathbf{p} \cdot \mathbf{x}_i) \right|^2 \quad (3.4)$$

for almost all configurations $\mathbf{x}_1 \cdots \mathbf{x}_N$. The "exceptional" configurations for which formulas such as (3.4) may fail will be ignored since they form a set of zero measure and therefore do not affect the configurational integral in (1.11). Let δ be any positive number. Since $\Phi(\mathbf{p})$ is¹² a continuous function of $\mathbf{p}$, and $\Phi(0) \geq 0$, we can find a positive number p_0 (depending on δ) such that

$$\Phi(\mathbf{p}) \geq (1 - \delta)\Phi(0) \quad (3.5)$$

whenever p is inside a cube of side $2p_0$ centered at the origin. Since $\Phi(\mathbf{p}) \geq 0$ when $\mathbf{p}$ is outside this cube, it follows from (4) that

$$W + \frac{1}{2}N\gamma'\varphi(0) \geq \frac{1}{2}(1 - \delta)\Phi(0)\gamma' \times \int d\mathbf{p} \left| \Psi(\mathbf{p}) \sum_{i=1}^N \exp(2\pi i\gamma\mathbf{p} \cdot \mathbf{x}_i) \right|^2 \quad (3.6)$$

where

$$\Psi(\mathbf{p}) \equiv \begin{cases} \prod_{n=1}^r (1 - |p_n|/p_0) & \text{if } |p_n| < p_0 \text{ for all } n, \\ 0 & \text{otherwise,} \end{cases} \quad (3.7)$$

and $p_1 \cdots p_r$ are the components of the vector $\mathbf{p}$. Applying Parseval's theorem to (6) we obtain

$$W + \frac{1}{2}N\gamma'\varphi(0) \geq (1 - \delta)\Phi(0)\frac{1}{2}\gamma' \times \int d(\gamma\mathbf{x}) \left\{ \sum_{i=1}^N \psi[\gamma(\mathbf{x} - \mathbf{x}_i)] \right\}^2 \quad (3.8)$$

where

$$\begin{aligned} \psi(\mathbf{y}) &\equiv \int \Psi(\mathbf{p}) \exp(-2\pi i\mathbf{p} \cdot \mathbf{y}) d\mathbf{p} \\ &= \prod_{n=1}^r \frac{\sin^2(\pi y_n p_0)}{\pi^2 y_n^2 p_0} \end{aligned} \quad (3.9)$$

and $y_1 \cdots y_r$ are the components of the vector $\mathbf{y}$.

A lower bound on the integral in (8) can be obtained by confining the integration to a cube Ω^* concentric with Ω and similarly oriented but having

¹² This follows from the existence of $\int |\varphi(\mathbf{x})| d\mathbf{x}$.

a side of length $\Omega^{1/r} + l$ where l is an arbitrary positive quantity. Applying the Schwartz inequality to the resulting integral and writing Ω^* for the volume of the cube Ω^* we obtain

$$\begin{aligned} W + \frac{1}{2}N\gamma'\varphi(0) &\geq \frac{1}{2}(1 - \delta)\Phi(0) \left[\sum_{i=1}^N \int_{\Omega^*} \psi[\gamma(\mathbf{x} - \mathbf{x}_i)] d(\gamma\mathbf{x}) \right]^2 / \Omega^* \\ &\geq \frac{1}{2}(1 - \delta)\Phi(0) \left[N \int_{v < \gamma l} \psi(\mathbf{y}) d\mathbf{y} \right]^2 / \Omega^* \end{aligned} \quad (3.10)$$

since the integrand is nonnegative and every point $\mathbf{x}$ inside the sphere $|\mathbf{x} - \mathbf{x}_i| < l$ is also within Ω^* .

Let us choose l so that $l \rightarrow \infty$ and $l/\Omega^{1/r} \rightarrow 0$ in the thermodynamic limit; for example, we may take $l \propto \Omega^{1/2r}$. Then in this limit we have $\Omega^*/\Omega \rightarrow 1$ and $\int_{v < \gamma l} \psi(\mathbf{y}) d\mathbf{y} \rightarrow 1$, and the lower bound on W/Ω implied by (10) has the thermodynamic limit $-\frac{1}{2}\rho\gamma'\varphi(0) + \frac{1}{2}(1 - \delta)\Phi(0)\rho^2$.

Since this result holds for arbitrarily small δ , it is also true in the limit $\delta \rightarrow 0$; that is to say, there exists a sequence of lower bounds on W , call them $W_{\min}$, with the property¹³

$$\begin{aligned} \lim_{\Omega \rightarrow \infty} W_{\min}/\Omega &= -\frac{1}{2}\rho\gamma'\varphi(0) + \frac{1}{2}\Phi(0)\rho^2 \\ &= -\frac{1}{2}\rho\gamma'\varphi(0) + \frac{1}{2}\alpha\rho^2 \end{aligned} \quad (3.11)$$

in the notation of (1.8).

This result enables us to take the thermodynamic limit of (3), obtaining

$$a(\rho, \gamma) \geq a^0(\rho) - \frac{1}{2}\rho\gamma'\varphi(0) + \frac{1}{2}\alpha\rho^2 \quad (3.12)$$

for nonnegative-definite potentials. In the van der Waals limit this formula reduces to

$$a(\rho, 0+) \geq a^0(\rho) + \frac{1}{2}\alpha\rho^2 \quad (3.13)$$

which when combined with (2.24) gives

$$a(\rho, 0+) = a^0(\rho) + \frac{1}{2}\alpha\rho^2 \quad (3.14)$$

for nonnegative-definite Kac potentials.

IV. LOWER BOUND ON THE FREE ENERGY: NONPOSITIVE KAC POTENTIALS

Another case where a lower bound on the free energy can be found fairly easily arises when the Kac potential is nonpositive; that is when

$$\varphi(\mathbf{x}) \leq 0 \quad \text{for all } \mathbf{x}. \quad (4.1)$$

In this case it is again necessary to divide the cube Ω into cubical cells $\omega_1 \cdots \omega_M$, each of side $s + t$

¹³ A proof of (3.11) for systems with periodic boundary conditions was given by E. Lieb, Phys. Rev. **130**, 2518 (1963). We are indebted to E. Newman and M. Austin for advice on the proof presented here.

(see Fig. 2). The definition (1.11) of the partition function may be written

$$Z(N, \Omega, \gamma) = \sum_{N_1 \dots N_M} Z(N_1, \dots, N_M) \quad (4.2)$$

where the sum is over all sets of M nonnegative integers adding up to N and $Z(N_1, \dots, N_M)$ means the contribution to (1.11) from configurations with exactly N_i particles in cell ω_i ($i = 1, 2 \dots M$). Since there are $(N + M - 1)!/N!(M - 1)!$ terms in the sum it has the upper bound

$$Z(N, \Omega, \gamma) \leq [(N + M - 1)!/N!(M - 1)!] \times \max_{N_1 \dots N_M} Z(N_1, \dots, N_M), \quad (4.3)$$

the maximum being taken over all sets of nonnegative integers $N_1 \dots N_M$ which add up to N . The combinatorial argument which led to (2.2) gives, when applied to $Z(N_1, \dots, N_M)$, the formula

$$Z(N_1, \dots, N_M) = \prod_i [(1/N_i!)(m/2\pi\hbar^2\beta)^{N_i/2}] \times \int_{\omega_1} \dots \int_{\omega_M} e^{-\beta V} d\mathbf{x}_1 \dots d\mathbf{x}_N \quad (4.4)$$

where the first N_1 of the N integrations are over the cell ω_1 , [not ω'_i as in (2.2)] the next N_2 over ω_2 , and so on.

To obtain an upper bound on the integral in (4) we separate the potential energy V into three parts:

$$V = Q' + \tilde{Q} + W \quad (4.5)$$

where Q' is the contribution to V from short-range interactions between particles that are in the same cell, $\tilde{Q}$ the contribution from short-range interactions between particles that are in different cells, and W is the total contribution from long-range interactions. If $\tilde{Q}_{\min}$ and $W_{\min}$ are lower bounds on $\tilde{Q}$ and W , then (4) and (5) lead to the inequality, analogous to (2.4),

$$Z(N_1, \dots, N_M) \leq \left\{ \prod_i Z^0(N_i, \omega) \right\} \times \exp [-(\tilde{Q}_{\min} + W_{\min})/kT] \quad (4.6)$$

where $Z^0(N_i, \omega)$ is the partition function for N_i particles of the reference system in a cube of side $s + t$.

To find a suitable lower bound on $\tilde{Q}$, we split it into two parts:

$$\tilde{Q} = Q'' + Q''' \quad (4.7)$$

where Q'' is, as in (2.5), the contribution to $\tilde{Q}$ from pairs of particles whose centers are both within the inner cells of side s denoted by ω'_i ($i = 1, 2 \dots M$) in Sec. 2, and Q''' is the contribution of pairs of

particles, at least one of which is in the "corridor" consisting of points that are not in any of the ω'_i (see Fig. 2). The argument used to prove (2.9) proves at the same time that

$$Q'' \geq -\frac{1}{2} D_2 N N_{\max} J_s t^{-r-s}. \quad (4.8)$$

The contribution Q''' has the lower bound

$$Q''' \geq -N_{\text{corr}} \Phi' \quad (4.9)$$

where $-\Phi'$ is a lower bound on the interaction of a given particle with all its neighbors, whose existence is a consequence¹⁴ of (1.20), and N_{corr} is the number of particles in the corridor. It can be shown¹⁵ that the number of particles in a given region, multiplied by the reciprocal close-packing density ρ_o^{-1} , does not exceed the volume occupied by all points whose distance from the region is at most r_o . Hence, $N_{\max}$ and N_{corr} have (provided $s \geq 2r_o$) the upper bounds

$$N_{\max} \rho_o^{-1} < (s + 2r_o)^r \quad (4.10)$$

$$\begin{aligned} N_{\text{corr}} \rho_o^{-1} &\leq (\Omega^{1/r} + 2r_o)^r - M(s - 2r_o)^r \\ &= M\{(s + t + 2r_o M^{-1/r})^r - (s - 2r_o)^r\} \\ &\leq \nu M(s + t + 2r_o M^{-1/r})^{r-1} \\ &\quad \times [t + 2r_o(1 + M^{-1/r})] \end{aligned} \quad (4.11)$$

by (2.1) and (2.17).

Substituting (10) and (11) into (7), (8), and (9), we obtain

$$\tilde{Q} \geq \tilde{Q}_{\min}, \quad (4.12)$$

where

$$\begin{aligned} \tilde{Q}_{\min} &= -\frac{1}{2} D_2 N \rho_o (s + 2r_o)^r J_s t^{-r-s} \\ &\quad - \rho_o \nu M (s + t + 2r_o M^{-1/r})^{r-1} \\ &\quad \times [t + 2r_o(1 + M^{-1/r})] \Phi'. \end{aligned} \quad (4.13)$$

The details of this formula are unimportant; all that is important is its behavior under the triple limiting process described in the introduction. This behavior is

$$\begin{aligned} \lim_{s \rightarrow \infty} \lim_{\gamma \rightarrow 0} \lim_{\Omega \rightarrow \infty} (\tilde{Q}_{\min}/\Omega) \\ &= \lim_{s \rightarrow \infty} \lim_{\gamma \rightarrow 0} \left\{ -\frac{1}{2} D_2 \rho \rho_o (s + 2r_o)^r J_s t^{-r-s} \right. \\ &\quad \left. - \nu (s + t)^{-1} (t + 2r_o) \Phi' \right\} \\ &= 0 \end{aligned} \quad (4.14)$$

by (2.1) and (2.22).

¹⁴ O. Penrose, J. Math. Phys. 4, 1312 (1963).

¹⁵ O. Penrose, Phys. Letters 11, 224 (1964).

A simple lower bound on W , the total long-range interaction, is given by

$$W \geq \frac{1}{2} \sum_i \sum_j N_i N_j w_{\min}(\mathbf{k}_{ij}) \quad (4.15)$$

where

$$w_{\min}(\mathbf{k}_{ij}) \equiv \min_{\substack{\mathbf{x} \in \omega_i \\ \mathbf{y} \in \omega_j}} w(\mathbf{x} - \mathbf{y}, \gamma) = \min_{\mathbf{r} \in \omega_0} w(\mathbf{k}_{ij} + 2\mathbf{r}, \gamma). \quad (4.16)$$

the γ -dependence of $w_{\min}(\mathbf{k})$ not being explicitly shown. These formulas are analogous to (2.6) and (2.7) but the $i = j$ terms are now included. Since $N_i N_j \leq \frac{1}{2} N_i^2 + \frac{1}{2} N_j^2$, and $w_{\min}(\mathbf{k}_{ij}) \leq 0$ by (1), we may deduce from (4.15) the inequality

$$W \geq -\frac{1}{2} \sum_i \sum_j (\frac{1}{2} N_i^2 + \frac{1}{2} N_j^2) |w_{\min}(\mathbf{k}_{ij})| \\ = -\frac{1}{2} \sum_i N_i^2 \sum_j |w_{\min}(\mathbf{k}_{ij})|. \quad (4.17)$$

The sum over j may be extended, without destroying the validity of (17), to include the infinite network of cells continuing outside Ω the pattern established inside it by the cells $\omega_1 \cdots \omega_M$. In the notation of (2.14) the resulting inequality is $W \geq W_{\min}$ with

$$W_{\min} = \frac{1}{2} \sum_i N_i^2 \sum_{\mathbf{k}} w_{\min}(\mathbf{k}). \quad (4.18)$$

Substituting this into (6) and using (3) and (1.10), we obtain

$$A(N, \Omega, \gamma) \geq kT \log [N! (M-1)! / (N+M-1)!] \\ + \min_{N_1, \dots, N_M} \sum_{i=1}^M \{A^0(N_i, \omega) \\ + \frac{1}{2} N_i^2 \sum_{\mathbf{k}} w_{\min}(\mathbf{k})\} + \tilde{Q}_{\min}. \quad (4.19)$$

The second term on the right can be simplified by means of a simple property of the convex envelope of a function, defined in (2.27). This property is

$$M^{-1} \sum_{i=1}^M f(N_i) \geq M^{-1} \sum_i \text{CE} \{f(N_i)\} \\ \geq \text{CE} \{f(M^{-1} \sum_i N_i)\} \quad (4.20)$$

where the first inequality follows from the fact that $\text{CE} \{f\}$ is a lower bound on f , and the second from the fact that $\text{CE} \{f\}$ is convex.

Using (4.20) in (4.19) we obtain

$$A(N, \Omega, \gamma) \geq kT \log [N! (M-1)! / (N+M-1)!] \\ + M \text{CE} \{A^0(N/M, \omega) \\ + \frac{1}{2} (N/M)^2 \sum_{\mathbf{k}} w_{\min}(\mathbf{k})\} + \tilde{Q}_{\min} \quad (4.21)$$

where $\text{CE} \{ \}$ is the convex envelope of the quantity in braces regarded as a function of N/M .

To apply the triple limiting process described in Sec I we first divide (4.21) by Ω and take the thermodynamic limit $\Omega \rightarrow \infty$, using Stirling's approximation for the factorials. In the notation of (1.13) the result is

$$a(\rho, \gamma) \geq -kT \{(s+t)^{-\gamma} \log [1 + \rho(s+t)^{\gamma}] \\ + \rho \log [1 + \rho^{-1}(s+t)^{-\gamma}]\} \\ + \text{CE} \{(s+t)^{-\gamma} A^0(\rho(s+t)^{\gamma}, \omega) \\ + \frac{1}{2} \rho^2 (s+t)^{\gamma} \sum w_{\min}(\mathbf{k})\} + \lim_{\Omega \rightarrow \infty} \tilde{Q}_{\min}/\Omega \quad (4.22)$$

since

$$N/M = \rho \Omega / M = \rho(s+t)^{\gamma}.$$

In order to carry through the other two limit processes we require the following lemma:

Let $f_n(\xi)$ be a sequence of functions converging uniformly on an interval to $f(\xi)$ as $n \rightarrow \infty$; then we have

$$\lim_{n \rightarrow \infty} \text{CE} \{f_n(\xi)\} = \text{CE} \{f(\xi)\}. \quad (4.23)$$

Proof: Given any $\delta > 0$ there exists an $\mathfrak{N}$ such that for $n \geq \mathfrak{N}$, $|f_n(\xi) - f(\xi)| < \delta$ for all ξ in the interval. We then have from the definition (2.26) of the convex envelope

$$\text{CE} \{f_n(\xi)\} \geq \text{CE} \{f(\xi)\} - \delta$$

for all ξ in the interval and $n \geq \mathfrak{N}$

since $\text{CE} \{f(\xi)\} - \delta$ is a convex function which is $\leq f_n(\xi)$. Similarly

$$\text{CE} \{f(\xi)\} \geq \text{CE} \{f_n(\xi)\} - \delta$$

for all ξ in the interval and $n \geq \mathfrak{N}$.

Hence

$$|\text{CE} \{f_n(\xi)\} - \text{CE} \{f(\xi)\}| \leq \delta$$

for all ξ in the interval and $n \geq \mathfrak{N}$

which, since δ is arbitrary, proves the lemma. Q.E.D.

In our case we consider an interval, $0 \leq \rho \leq \rho_1 < \rho_0$ where ρ_1 is any density less than the close packing density ρ_0 . Taking the limit $\gamma \rightarrow 0$ of (22) we obtain

$$a(\rho, 0+) \geq -kT \{(s+t)^{-\gamma} \log [1 + \rho(s+t)^{\gamma}] \\ + \rho \log [1 + \rho^{-1}(s+t)^{-\gamma}]\} \\ + \text{CE} \{(s+t)^{-\gamma} A^0[\rho(s+t)^{\gamma}, \omega] \\ + \frac{1}{2} \alpha \rho^2\} + \lim_{\Omega \rightarrow \infty} \tilde{Q}_{\min}/\Omega \quad (4.24)$$

since, by an argument like that which led to (2.20),

$$(s+t)^r \lim_{\gamma \rightarrow 0} \sum_{\mathbf{k}} w_{\min}(\mathbf{k}) = \int \varphi(\mathbf{x}) d\mathbf{x} \equiv \alpha$$

and the convergence is uniform because the difference between the sum and the integral is independent of ρ . Finally, taking the limit $s \rightarrow \infty$, where the convergence is again uniform (Sec. 7k of Ref. 7), and using (14), we obtain

$$a(\rho, 0+) \geq \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\}. \quad (4.25)$$

Combined with (2.25) this gives

$$a(\rho, 0+) = \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\} \quad (4.26)$$

for nonpositive Kac potentials. The result obtained by Kac, Uhlenbeck, and Hemmer⁶ is an example of (4.26).

V. LOWER BOUND TO THE FREE ENERGY: MORE GENERAL KAC POTENTIALS

When the Kac potential is neither nonnegative-definite nor nonpositive, a lower bound can still be obtained, though the method is more complicated than before. We express $\Phi(\mathbf{p})$, the ν -dimensional Fourier transform of $\varphi(\mathbf{x})$ defined in (3.1) as the sum of two parts

$$\Phi(\mathbf{p}) = \Phi_+(\mathbf{p}) + \Phi_-(\mathbf{p}) \quad (5.1)$$

so chosen that

$$\left. \begin{aligned} \Phi_+(\mathbf{p}) &\geq 0 \quad \text{for all } \mathbf{p}, \\ \Phi_-(0) &= \text{Min}_p \Phi_-(\mathbf{p}) = \min_p \Phi(\mathbf{p}) \equiv \Phi_{\min}, \\ \int \Phi_{\pm}(\mathbf{p}) d\mathbf{p} &< \infty, \\ \Phi_{\pm}(\mathbf{p}) &\text{ is continuous.} \end{aligned} \right\} \quad (5.2)$$

The inverse transforms of $\Phi_+(\mathbf{p})$ and $\Phi_-(\mathbf{p})$ will be denoted by $\varphi_+(\mathbf{x})$ and $\varphi_-(\mathbf{x})$ and we shall require also that $\varphi_+(\mathbf{x})$ and $\varphi_-(\mathbf{x})$ satisfy (1.21). These conditions can be satisfied (provided $d\Phi/dp_n > -\infty$ at $p = 0$) by taking

$$\Phi_+(\mathbf{p}) = \begin{cases} [\Phi(0) - \Phi_{\min}](1 - p/p')^n & \text{if } p \leq p' \\ 0 & \text{if } p \geq p' \end{cases} \quad (5.3)$$

where p' is the smallest value of p at which $\Phi(\mathbf{p})$ attains its minimum value $\Phi_{\min}$ and n is a positive integer (≥ 2) chosen sufficiently large to make $(1 - p/p')^n \leq [\Phi(\mathbf{p}) - \Phi_{\min}]/[\Phi(0) - \Phi_{\min}]$, for $p \leq p'$. When $\Phi_+(\mathbf{p})$ is given by (3) $\varphi_+(\mathbf{x})$ can be computed explicitly and shown to satisfy (1.21), and hence so will $\varphi_-(\mathbf{x})$. [Even when $d\Phi/dp = -\infty$ at

$p = 0$ there is every reason to believe that the division of Φ into Φ_+ and Φ_- can be made in a way to satisfy all our conditions, provided $\varphi(\mathbf{x})$ satisfies (1.21).]

Since $\varphi_+(\mathbf{x})$ is a nonnegative-definite function its contribution to W , which may be written W_+ , can be estimated by the method used in Sec. III. In analogy with (3.11), the result has the form $W_+ \geq W_{+, \min}$ where

$$\lim_{\Omega \rightarrow \infty} W_{+, \min}/\Omega = -\frac{1}{2}\rho\gamma^r\varphi_+(0) + \frac{1}{2}\Phi_+(0)\rho^2. \quad (5.4)$$

The other contribution W_- has a lower bound analogous to (4.15)

$$W_- \geq \frac{1}{2} \sum_i \sum_j N_i N_j w_{-, \min}(\mathbf{k}_{ij}) \quad (5.5)$$

where as in (4.16) $\mathbf{k}_i$ is the position vector from the center of the cell ω_i to that of ω_j , and

$$\begin{aligned} w_{-, \min}(\mathbf{k}_{ij}) &\equiv \text{Min}_{\substack{\mathbf{x} \in \omega_i \\ \mathbf{y} \in \omega_j}} w_-(\mathbf{x} - \mathbf{y}, \gamma) \\ &= \text{Min}_{\mathbf{r} \in \omega_0} w_-(\mathbf{k}_{ij} + 2\mathbf{r}, \gamma), \end{aligned} \quad (5.6)$$

where $w_-(\mathbf{x}, \gamma) = \gamma^r\varphi_-(\gamma\mathbf{x})$ and ω_0 is a cube of side $s+t$ centered at the origin.

The quadratic form in (5) can be diagonalized using a Fourier transformation. We define the function

$$W(\mathbf{p}) \equiv \sum_{\mathbf{k}} w_{-, \min}(\mathbf{k}) \exp(2\pi i \mathbf{p} \cdot \mathbf{k}) \quad (5.7)$$

where the sum goes over all the different values taken by the vector $\mathbf{k}_{ij}$ as both i and j range over the values 1, 2, $\dots$ M . These values lie on a simple cubic lattice of spacing $s+t$ with a lattice point at the origin and are inside (not on the surface of) a cube of volume $2^r\Omega$ centered at the origin. The sum in (7) therefore covers just $[2\Omega^{1/r}(s+t)^{-1} - 1] = [2M^{1/r} - 1]^r \equiv M'$ lattice points. The function $W(\mathbf{p})$ is periodic in $\mathbf{p}$, the unit cell of the periodicity being a cube of side $(s+t)^{-1}$. Although the notation does not show it, $W(\mathbf{p})$ depends on $s+t$, γ , and Ω as well as on $\mathbf{p}$.

The inverse of (7) is

$$w_{-, \min}(\mathbf{k}) = (M')^{-1} \sum_{\mathbf{p}} W(\mathbf{p}) \exp(-2\pi i \mathbf{p} \cdot \mathbf{k}) \quad (5.8)$$

where the sum goes over M' values of $\mathbf{p}$ lying inside a cube of side $(s+t)^{-1}$ and on a lattice of spacing $(M')^{-1/r}(s+t)^{-1} = [2\Omega^{1/r} - (s+t)^{-1}]$. Substituting (8) into (5) and rearranging, we obtain

$$W_- \geq \frac{1}{2}(M')^{-1} \sum_{\mathbf{p}} W(\mathbf{p}) |n(\mathbf{p})|^2 \quad (5.9)$$

where

$$n(\mathbf{p}) \equiv \sum_{i=1}^M N_i \exp(2\pi i \mathbf{p} \cdot \mathbf{k}_i) \quad (5.10)$$

and $\mathbf{k}_i$ is the position vector of the center of ω_i . For a lower bound on the sum (9) we may replace $W(\mathbf{p})$ by its minimum value, obtaining

$$\begin{aligned} W_- &\geq \frac{1}{2}(M')^{-1} \sum_{\mathbf{p}} |n(\mathbf{p})|^2 \text{Min}_{\mathbf{p}} W(\mathbf{p}) \\ &= \frac{1}{2} \sum_{i=1}^M N_i^2 \text{Min}_{\mathbf{p}} W(\mathbf{p}). \end{aligned} \quad (5.11)$$

Substituting this result into (4.6) and using (4.3) and (1.10) we obtain

$$\begin{aligned} A(N, \Omega, \gamma) &\geq kT \log [N! (M-1)! / (N+M-1)!] \\ &+ \text{Min}_{N_1 \dots N_M} \sum_{i=1}^M \{A^0(N_i, \omega) \\ &+ \frac{1}{2} N_i^2 \text{Min}_{\mathbf{p}} W(\mathbf{p})\} + W_{+, \min} + \tilde{Q}_{\min} \end{aligned} \quad (5.12)$$

where $W_{+, \min}$ satisfies (4).

The inequality (12) is very similar to (4.19) and the effect on it of the triple limit process can be studied by the method used for (4.19). The result, analogous to (4.25), is

$$\alpha(\rho, 0+) \geq \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha_- \rho^2\} + \frac{1}{2}\alpha_+ \rho^2, \quad (5.13)$$

where

$$\begin{aligned} \alpha_+ &\equiv (2/\rho^3) \lim_{\Omega \rightarrow \infty} \lim_{\gamma \rightarrow 0} \lim_{\Omega \rightarrow \infty} W_{+, \min} / \Omega \\ &= \Phi_+(0) \end{aligned} \quad (5.14)$$

by (4), and

$$\alpha_- \equiv \lim_{\Omega \rightarrow \infty} \lim_{\gamma \rightarrow 0} \lim_{\Omega \rightarrow \infty} (s+t)' \text{Min}_{\mathbf{p}} W(\mathbf{p}). \quad (5.15)$$

The first step is to carry out the limit process $\Omega \rightarrow \infty$ in (15). It follows from the definition (7) that

$$|W(\mathbf{p}) - \lim_{\Omega \rightarrow \infty} W(\mathbf{p})| \leq \sum |w_{-, \min}(\mathbf{k})| \quad (5.16)$$

where the sum is over all lattice points $\mathbf{k}$ outside a cube of volume just less than $2^3\Omega$ centered at the origin. This sum is independent of $\mathbf{p}$, and because of (1.21) it tends to zero as $\Omega \rightarrow \infty$. Therefore $W(\mathbf{p})$ approaches its limit, as $\Omega \rightarrow \infty$ uniformly in $\mathbf{p}$, so that

$$\begin{aligned} \lim_{\Omega \rightarrow \infty} \text{Min}_{\mathbf{p}} W(\mathbf{p}) &= \text{Min}_{\mathbf{p}} \lim_{\Omega \rightarrow \infty} W(\mathbf{p}) \\ &= \text{Min}_{\mathbf{p}} \sum_{\mathbf{p}} (\mathbf{p}, \gamma) \end{aligned} \quad (5.17)$$

where

$$\sum (\mathbf{p}, \gamma) \equiv \sum_{\mathbf{k}} w_{-, \min}(\mathbf{k}) \exp(2\pi i \mathbf{p} \cdot \mathbf{k}), \quad (5.18)$$

the sum going over an infinite lattice with spacing $s+t$.

To study the effect of the next limit process, $\gamma \rightarrow 0$, we consider separately the cases where $\mathbf{p}$ is inside and outside a cube Γ of side $2p_0$ centered at the origin. The dependence of p_0 on γ will be chosen so that in the limit $\gamma \rightarrow 0$ the sum (18) may be replaced by an integral if $\mathbf{p} \in \Gamma$ and by zero otherwise.

By writing $\gamma \mathbf{q}$ for $\mathbf{p}$ and $\mathbf{x}$ for $\gamma \mathbf{k}$ in (18), and using an argument similar to that which gave (2.20), we find that

$$\begin{aligned} (s+t)' \lim_{\gamma \rightarrow 0} \sum (\gamma \mathbf{q}, \gamma) \\ = \int \varphi_-(\mathbf{x}) \exp(2\pi i \mathbf{q} \cdot \mathbf{x}) d\mathbf{x} \\ = \Phi_-(\mathbf{q}). \end{aligned} \quad (5.19)$$

In order to use this result in (15), we must show also that the convergence to the limit is uniform provided $\gamma \mathbf{q} \in \Gamma$. To do this we use the definitions (3.1), (1.6), (18), and (6), to obtain the estimate

$$\begin{aligned} |\Phi(\mathbf{p}/\gamma) - (s+t)' \sum (\mathbf{p}, \gamma)| \\ = \left| \sum_{\mathbf{k}} \int_{\omega_0} e^{2\pi i \mathbf{p} \cdot \mathbf{k}} [e^{2\pi i \mathbf{p} \cdot \mathbf{y}} w_-(\mathbf{k} + \mathbf{y}, \gamma) \right. \\ \left. - \text{Min}_{\mathbf{z} \in \omega_0} w_-(\mathbf{k} + 2\mathbf{z}, \gamma)] d\mathbf{y} \right| \\ \leq \sum_{\mathbf{k}} \int_{\omega_0} \{|e^{2\pi i \mathbf{p} \cdot \mathbf{y}} - 1| |w_-(\mathbf{k} + \mathbf{y}, \gamma)| \\ + |w_-(\mathbf{k} + \mathbf{y}, \gamma) - \text{Min}_{\mathbf{z} \in \omega_0} w_-(\mathbf{k} + 2\mathbf{z}, \gamma)|\} d\mathbf{y} \\ \leq \pi p_0 (s+t) \int |w_-(\mathbf{x}, \gamma)| d\mathbf{x} \\ + \left| \int w_-(\mathbf{x}, \gamma) d\mathbf{x} - (s+t)' \sum_{\mathbf{k}} w_{-, \min}(\mathbf{k}) \right|. \end{aligned} \quad (5.20)$$

Since we have required that $\int |\varphi_-(\mathbf{y})| d\mathbf{y} < \infty$, the first part of the last member of (20) tends to zero with γ provided that

$$\lim_{\gamma \rightarrow 0} p_0 = 0. \quad (5.21)$$

The second part also tends to zero with γ , as in the argument leading to (2.20), because of the Riemann integrability of φ_- . Since both parts are independent of $\mathbf{p}$, the convergence to the limit in (19) is indeed uniform for $\gamma \mathbf{q} \in \Gamma$, and it follows that

$$\begin{aligned}
(s+t)' \lim_{\gamma \rightarrow 0} \min_{\mathbf{p} \in \Gamma} \sum (\mathbf{p}, \gamma) &= \lim_{\gamma \rightarrow 0} \text{Min}_{\mathbf{p} \in \Gamma} \Phi_{-}(\mathbf{p}/\gamma) \\
&= \text{Min}_{\mathbf{q}} \Phi_{-}(\mathbf{q}) \equiv \Phi_{-}(0)
\end{aligned}
\quad (5.22)$$

by (2), provided $\lim_{\gamma \rightarrow 0} p_0/\gamma = \infty$.

To complete the estimates of $\text{Min} \sum (\mathbf{p}, \gamma)$ for (18) we must also find a lower bound for $\sum (\mathbf{p}, \gamma)$ with $\mathbf{p}$ outside Γ . Whenever $\mathbf{p}$ is outside Γ , we can find a direction parallel to an edge of the cube Γ such that the component of $\mathbf{p}$ along this direction exceeds p_0 . If $\mathbf{l}$ denotes a vector of length $s+t$ along this direction we therefore have

$$p_0(s+t) \leq \mathbf{p} \cdot \mathbf{l} \leq \frac{1}{2}, \quad (5.23)$$

the second inequality being a consequence of the fact [see (8)] that all the allowed values of $\mathbf{p}$ lie inside a cube of side $(s+t)^{-1}$ centered at the origin. On multiplying both sides of (18) by $1 - \exp(2\pi i \mathbf{p} \cdot \mathbf{l})$ and taking absolute values, we obtain, since $|\mathbf{l}| = s+t$,

$$\begin{aligned}
2 \sin(\pi \mathbf{p} \cdot \mathbf{l}) |\sum (\mathbf{p}, \gamma)| &= |\sum_{\mathbf{k}} [w_{-, \min}(\mathbf{k}) - w_{-, \min}(\mathbf{k} - \mathbf{l})] \exp(2\pi i \mathbf{p} \cdot \mathbf{k})| \\
&\leq \sum_{\mathbf{k}} |w_{-, \min}(\mathbf{k}) - w_{-, \min}(\mathbf{k} - \mathbf{l})| \\
&\leq \sum_{\mathbf{k}} \text{Max}_{\mathbf{x} \in \omega_0} w_{-}(\mathbf{k} + 4\mathbf{x}, \gamma) \\
&\quad - \sum_{\mathbf{k}} \text{Min}_{\mathbf{x} \in \omega_0} w_{-}(\mathbf{k} + 4\mathbf{x}, \gamma)
\end{aligned}
\quad (5.24)$$

where ω_0 denotes, as in (6), a cube of side $(s+t)$ centered at the origin. Applying once more an argument of the type which led to (2.20), we find that both sums in the last member of (24) tend to the same integral in the limit $\gamma \rightarrow 0$. Thus (24) can be written in the form

$$|\sum (\mathbf{p}, \gamma)| \leq \frac{1}{2} |\csc(\pi \mathbf{p} \cdot \mathbf{l})| \delta(\gamma) \quad (5.25)$$

where δ does not depend on $\mathbf{p}$ and tends to 0 with γ . Combining (23) and (25) we obtain

$$|\sum (\mathbf{p}, \gamma)| \leq \delta(\gamma)/4p_0(s+t) \quad \text{for } \mathbf{p} \text{ outside } \Gamma \quad (5.26)$$

since $\sin x \geq 2x/\pi$ for $0 \leq x \leq \pi/2$. Let us now choose p_0 in such a way that

$$\lim_{\gamma \rightarrow 0} \delta(\gamma)/p_0 = 0. \quad (5.27)$$

This is compatible with the previous requirements (5.21) and $\lim p_0/\gamma = \infty$; for example, the choice $p_0 \propto [\gamma + \delta(\gamma)]^{1/2}$ satisfies all three requirements. Combining (27) and (26) we obtain

$$\lim_{\gamma \rightarrow 0} \text{Min}_{\mathbf{p} \text{ outside } \Gamma} \sum (\mathbf{p}, \gamma) = 0. \quad (5.28)$$

Combining (15) and (17) and then using (22) and (28), we obtain

$$\begin{aligned}
\alpha_{-} &= \lim_{s \rightarrow \infty} \lim_{\gamma \rightarrow 0} (s+t)' \text{Min}_{\mathbf{p}} \sum (\mathbf{p}, \gamma) \\
&= \lim_{s \rightarrow \infty} \Phi_{-}(0) = \Phi_{-}(0) = \Phi_{\min}.
\end{aligned}
\quad (5.29)$$

This completes the evaluation of α_{-} .

Our main results (2.25) and (13) can be summarized in the formula

$$\begin{aligned}
\text{CE} \{a^0(\rho) + \frac{1}{2}\alpha_{-}\rho^2\} + \frac{1}{2}\alpha_{+}\rho^2 &\leq a(\rho, 0+) \\
&\leq \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\}.
\end{aligned}
\quad (5.30)$$

From (30) we can find $a(\rho, 0+)$ exactly provided the upper and lower bounds coincide. This can happen in two ways:

(i) Where $a^0(\rho) + \frac{1}{2}\alpha_{-}\rho^2$ coincides with its convex envelope, (e.g., if $\alpha_{-} = 0$), the function $a^0\rho + \frac{1}{2}\alpha\rho^2$ does so too since $\alpha = \alpha_{+} + \alpha_{-} \geq \alpha_{-}$; thus (30) implies

$$\begin{aligned}
a(\rho, 0+) &= \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\} = a^0(\rho) + \frac{1}{2}\alpha\rho^2 \\
&\text{if } a^0(\rho) + \frac{1}{2}\alpha_{-}\rho^2 = \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha_{-}\rho^2\}.
\end{aligned}
\quad (5.31)$$

In the special case $\alpha_{-} = 0$ this reduces to (3.14).

(ii) If $\alpha_{+} = 0$ then we have $\alpha = \alpha_{-}$ so that (30) reduces to

$$a(\rho, 0+) = \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\} \quad \text{if } \alpha_{+} = 0. \quad (5.32)$$

The result (4.26) is a special case of this, since (4.1) implies $\Phi(0) \leq \Phi(\mathbf{p})$ for all $\mathbf{p}$.

VI. EQUATION OF STATE

For a system with finite γ , the thermodynamic pressure $p(\rho, \gamma)$ is given^{7,9} by

$$\begin{aligned}
p(\rho, \gamma) &= -\partial(\rho^{-1}a(\rho, \gamma))/\partial(\rho^{-1}) \\
&= \rho \partial a(\rho, \gamma)/\partial \rho - a(\rho, \gamma),
\end{aligned}
\quad (6.1)$$

the differentiation being at constant γ and also at constant T , although the dependence on T is not explicit in the notation. Since $a(\rho, \gamma)$ is^{7,9} a convex function of ρ at constant γ the derivative on the right of (1) exists¹⁶ except on a countable set of values of ρ ; it seems likely that this countable set is in fact empty but no proof is known.

Taking the limit $\gamma \rightarrow 0$ on both sides of (6.1) we obtain

$$p(\rho, 0+) = \rho \lim_{\gamma \rightarrow 0} \partial a(\rho, \gamma)/\partial \rho - a(\rho, 0+). \quad (6.2)$$

To evaluate the right side of (2) we must show that the order of the operations $\gamma \rightarrow 0$ and $\partial/\partial \rho$

¹⁶ Ref. 10, p. 94.

can be reversed. To this end we use the inequality¹⁷ for the right- and left-hand derivatives of a convex function

$$\begin{aligned} [a(\rho - \epsilon, \gamma) - a(\rho)]/(-\epsilon) &\leq D_-a(\rho, \gamma) \\ &\leq D_+a(\rho, \gamma) \\ &\leq [a(\rho + \epsilon, \gamma) - a(\rho)]/\epsilon \end{aligned} \quad (6.3)$$

where

$$D_{\pm}a(\rho, \gamma) \equiv \lim_{\epsilon \rightarrow 0} [a(\rho \pm \epsilon, \gamma) - a(\rho, \gamma)]/(\pm\epsilon), \quad (6.4)$$

with ϵ an arbitrary positive number.

Taking the limit $\gamma \rightarrow 0$ on both sides of (3), followed by the limit $\epsilon \rightarrow 0$, we obtain

$$\begin{aligned} D_-a(\rho, 0+) &\leq \lim_{\gamma \rightarrow 0} D_-a(\rho, \gamma) \\ &\leq \lim_{\gamma \rightarrow 0} D_+a(\rho, \gamma) \leq D_+a(\rho, 0+). \end{aligned} \quad (6.5)$$

Hence if $a(\rho, 0+)$ is differentiable all four of these expressions are equal, so that $\lim_{\gamma \rightarrow 0} D_{\pm}a(\rho, \gamma)$ exists and is equal to $da(\rho, 0+)/d\rho$. Substituting this result into (2) we obtain

$$p(\rho, 0+) = (\rho d/d\rho - 1)a(\rho, 0+) \quad (6.6)$$

at all points where $a(\rho, 0+)$ is differentiable. Equation (6) can be interpreted geometrically by the statement that $-p(\rho, 0+)$ is the place where the tangent at ρ to the graph of $a(\rho, 0+)$ intercepts the a -axis.

Combining (6) with (5.31) or (5.32), we obtain

$$p(\rho, 0+) = (\rho d/d\rho - 1) \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\} \quad (6.7)$$

for all Kac potentials to which (5.31) or (5.32) applies, including nonnegative definite and non-positive potentials.

If the graph of $a(\rho, 0+) = \text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\}$ has a straight segment (see Fig. 3) then the geometrical interpretation of (6) shows that $p(\rho, 0+)$ is constant along this straight segment; and the chemical potential $[a(\rho, 0+) + p(\rho, 0+)]/\rho = da(\rho, 0+)/d\rho$ is also constant. This behavior of the thermodynamic functions characterizes a first-order phase transition.

Since the straight portion of the graph $\text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\}$ touches the graph $a^0(\rho) + \frac{1}{2}\alpha\rho^2$ at both ends, the quantity

$$\tilde{p}_{vdw}(\rho) \equiv (\rho d/d\rho - 1)(a^0(\rho) + \frac{1}{2}\alpha\rho^2) \quad (6.8)$$

takes the same value, call it p_{sat} , at the two ends of the phase transition region. Moreover, if ρ_l and

ρ_* are the abscissas of the two points of contact, then we have

$$\begin{aligned} \int_{\rho_*}^{\rho_l} [\tilde{p}_{vdw}(\rho) - p_{sat}] d(\rho^{-1}) \\ = \{-[a^0(\rho) + \frac{1}{2}\alpha\rho^2 + p_{sat}]\rho^{-1}\}_{\rho_*}^{\rho_l} \\ = \{(d/d\rho)[a^0(\rho) + \frac{1}{2}\alpha\rho^2]\}_{\rho_*}^{\rho_l} \end{aligned} \quad (6.9)$$

using (8) first as a definition of $\tilde{p}_{vdw}(\rho)$ and then to evaluate p_{sat} . Since the slopes of the graph $a^0(\rho) + \frac{1}{2}\alpha\rho^2$ at the two points of contact are equal, the expression (9) vanishes. This shows that ρ_l and ρ_* are related to $\tilde{p}_{vdw}(\rho)$ by Maxwell's equal-area construction (Fig. 1). The replacement of $a^0(\rho) + \frac{1}{2}\alpha\rho^2$ by its convex envelope is precisely equivalent to making Maxwell's modification (1.2) in the function $\tilde{p}_{vdw}(\rho)$ defined by (8).

For values of ρ where the upper and lower bounds of $a(\rho, 0+)$, in (5.30) do not coincide we still obtain bounds on $\lim_{\gamma \rightarrow 0} \partial a(\rho, \gamma)/\partial\rho$ and hence on $p(\rho, 0+)$ by an argument due to Fisher¹⁸: owing to the convexity of the graph of $a(\rho, 0+)$ its slope at $\rho = \rho_0$ must lie between the slopes of tangents to its upper bound crossing its lower bound at $\rho = \rho_0$.

A result similar to that obtained for the pressure holds also for the internal energy density

$$u(\beta, \rho, \gamma) = (\partial/\partial\beta)[\beta a(\beta, \rho, \gamma)]. \quad (6.10)$$

Since $-\beta a(\beta, \rho, \gamma)$ is convex in β we obtain, as in the derivation of (6),

$$u(\beta, \rho, 0+) = \partial/\partial\beta[\beta a(\beta, \rho, 0+)]. \quad (6.11)$$

Unfortunately we have been unable to prove any similar general statements about the specific heat and compressibility which correspond to second derivatives of the free-energy density. At sufficiently low densities, however, one can show that all the density derivatives of $p(\rho, \gamma)$ approach the corresponding derivatives of $p(\rho, 0+)$ by using Vitali's theorem together with the results of Lebowitz and Penrose¹⁹ for the convergence of virial expansions.

VII. THE PAIR DISTRIBUTION FUNCTION

In order to understand better the effect of the Kac potential on possible phase transitions in the reference system and in the van der Waals system, it is useful to study the two-body distribution function. (In this section we do not aim at such a high standard of rigor as in the earlier sections.)

¹⁸ M. E. Fisher, "Bounds for the Derivatives of the Free Energy and the Pressure of a Hard Core System near Close Packing" (to be published).

¹⁹ J. L. Lebowitz and O. Penrose, J. Math. Phys. 5, 841 (1964).

¹⁷ Obtained by making $\delta \rightarrow 0$ in Eq. (3.18.3) of Hardy, Littlewood and Polya (Ref. 10).

Instead of the usual two-body distribution function²⁰ $n_2(\mathbf{x}_1, \mathbf{x}_2)$, we shall study its space average

$$\bar{n}_2(\mathbf{r}) \equiv \Omega^{-1} \int n_2(\mathbf{x}, \mathbf{x} + \mathbf{r}) d\mathbf{x}. \quad (7.1)$$

This distribution function when the system has N particles in a box Ω and a Kac parameter γ will be denoted by $\bar{n}_2(\mathbf{r}; N, \Omega, \gamma)$. This function can be determined from the formula²¹

$$\begin{aligned} \frac{1}{2} \int \bar{n}_2(\mathbf{r}; N, \Omega, \gamma) q'(\mathbf{r}) d\mathbf{r} \\ = (\partial/\partial\eta) \Omega^{-1} A[N, \Omega, \gamma, \eta q'(\mathbf{r})]_{\eta=0} \end{aligned} \quad (7.2)$$

which holds for arbitrary bounded functions $q'(\mathbf{r})$. The integration may be taken over all space, since $\bar{n}_2(\mathbf{r}; N, \Omega, \gamma) = 0$ for large r . The symbol $A[N, \Omega, \gamma, \eta q'(\mathbf{r})]$ denotes the free energy analogous to (1.10) when the short-range interaction potential is not $q(\mathbf{r})$ but $q(\mathbf{r}) + \eta q'(\mathbf{r})$, and η is a parameter. Taking the thermodynamic limit and then the van der Waals limit in (2) we obtain, provided all the relevant limits and the derivative exist,

$$\begin{aligned} \frac{1}{2} \int \bar{n}_2(\mathbf{r}; \rho, 0+) q'(\mathbf{r}) d\mathbf{r} \\ = (\partial/\partial\eta) a[\rho, 0+, \eta q'(\mathbf{r})]_{\eta=0} \end{aligned} \quad (7.3)$$

where

$$\bar{n}_2(\mathbf{r}; \rho, 0+) \equiv \lim_{\gamma \rightarrow 0} \lim_{\Omega \rightarrow \infty} \bar{n}_2(\mathbf{r}; \rho\Omega, \Omega, \gamma) \quad (7.4)$$

and

$$\begin{aligned} a[\rho, 0+, \eta q'(\mathbf{r})] \\ = \lim_{\gamma \rightarrow 0} \lim_{\Omega \rightarrow \infty} A[\rho\Omega, \Omega, \gamma, \eta q'(\mathbf{r})]/\Omega. \end{aligned} \quad (7.5)$$

The permutation of the limit operations $\gamma \rightarrow 0$ and $\Omega \rightarrow \infty$ with integration and differentiation in deriving (3) is justified on the left by Lebesgue's theorem.²² On the right it is justified [as in the argument based on (6.3) and (6.5)], by the convexity of $A[N, \Omega, \gamma, \eta q'(\mathbf{r})]$ as a function of η . This convexity can be verified by calculating the second derivative of A with respect to η . In a similar way we can obtain

$$\frac{1}{2} \int \bar{n}_2^0(\mathbf{r}; \rho) q'(\mathbf{r}) d\mathbf{r} = (\partial/\partial\eta) a^0[\rho, \eta q'(\mathbf{r})]_{\eta=0} \quad (7.6)$$

²⁰ T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Sec. 29.

²¹ Equation (7.2) is the classical analog of a quantum formula given by Bogolyubov and Zubarev, *Zh. Eksp. i Teor. Fiz.* **28**, 129 (1955) [English transl.: *Soviet Phys.—JETP* **1**, 83 (1955)]. This was first used in this type of work by M. E. Fisher.

²² F. Riesz and B. Sz. Nagy, *Functional Analysis* (Frederick Ungar Publishing Company, New York, 1955), p. 37.

where the superscript zero denotes quantities belonging to the reference system with a modified short-range potential $q(\mathbf{r}) + \eta q'(\mathbf{r})$. When the conditions of validity for our main result (5.31) or (5.32) are satisfied, (3) reduces to

$$\begin{aligned} \frac{1}{2} \int \bar{n}_2(\mathbf{r}; \rho, 0+) q'(\mathbf{r}) d\mathbf{r} \\ = (\partial/\partial\eta) \text{CE} \{a^0[\rho, \eta q'(\mathbf{r})] + \frac{1}{2}\alpha\rho^2\}_{\eta=0}. \end{aligned} \quad (7.7)$$

Two cases may be distinguished. In the first of these the graph of $a^0[\rho, \eta q'(\mathbf{r})] + \frac{1}{2}\alpha\rho^2$ coincides with that of its convex envelope and so (7) combines with (6) to give

$$\frac{1}{2} \int \bar{n}_2(\mathbf{r}; \rho, 0+) q'(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \int \bar{n}_2^0(\mathbf{r}, \rho) q'(\mathbf{r}) d\mathbf{r} \quad (7.8)$$

which implies

$$\bar{n}_2(\mathbf{r}; \rho, 0+) = \bar{n}_2^0(\mathbf{r}, \rho) \quad (7.9)$$

since $q'(\mathbf{r})$ is arbitrary. In this case, therefore, the Kac potential does not affect the distribution of pairs of particles, as one might expect from (1.8).

In the alternative case, where the graph of $a^0[\rho, \eta q'(\mathbf{r})] + \frac{1}{2}\alpha\rho^2$ does not coincide with that of its convex envelope, the latter is a straight line touching the former at two places, say ρ_1 and ρ_2 . Both ρ_1 and ρ_2 depend, in general, on η . The equation of this straight line may be written

$$\begin{aligned} \text{CE} \{a^0[\rho, \eta q'(\mathbf{r})] + \frac{1}{2}\alpha\rho^2\} = [(\rho - \rho_1)a_2 \\ + (\rho_2 - \rho)a_1](\rho_2 - \rho_1)^{-1}(\rho_1 < \rho < \rho_2) \end{aligned} \quad (7.10)$$

where

$$a_h \equiv a^0[\rho_h, \eta q'(\mathbf{r})] + \frac{1}{2}\alpha\rho_h^2 \quad (h = 1, 2). \quad (7.11)$$

On substituting this into (7) and using (9), which applies when $\rho = \rho_1$ or $\rho = \rho_2$, we obtain

$$\begin{aligned} \frac{1}{2} \int \bar{n}_2(\mathbf{r}; \rho, 0+) q'(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \int \left[\frac{\rho - \rho_1}{\rho_2 - \rho_1} \bar{n}_2^0(\mathbf{r}; \rho_2) \right. \\ \left. + \frac{\rho_2 - \rho}{\rho_2 - \rho_1} \bar{n}_2^0(\mathbf{r}, \rho_1) \right] q'(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (7.12)$$

since

$$\begin{aligned} \frac{\partial}{\partial\rho_1} \left[\frac{(\rho - \rho_1)a_2 + (\rho_2 - \rho)a_1}{\rho_2 - \rho_1} \right] \\ = \frac{\rho_2 - \rho}{(\rho_2 - \rho_1)^2} \left[a_1 - a_2 + (\rho_2 - \rho_1) \frac{\partial}{\partial\rho_1} a_1 \right] \\ = 0, \text{ etc.} \end{aligned} \quad (7.13)$$

by virtue of the double tangent construction. [In Eq. (13) we are treating η , ρ_1 , ρ_2 , ρ as independent

variables.] Since $q'(\mathbf{r})$ is arbitrary, it follows from (12) that

$$\begin{aligned} \bar{n}_2(\mathbf{r}; \rho, 0+) &= \frac{\rho - \rho_1}{\rho_2 - \rho_1} \bar{n}_2^0(\mathbf{r}; \rho_2) \\ &+ \frac{\rho_2 - \rho}{\rho_2 - \rho_1} \bar{n}_2^0(\mathbf{r}; \rho_1), \quad (\rho_1 < \rho < \rho_2). \end{aligned} \quad (7.14)$$

This equation can be interpreted²³ to mean that two phases coexist whenever $\text{CE} \{a^0(\rho) + \frac{1}{2}\alpha\rho^2\} < a^0(\rho) + \frac{1}{2}\alpha\rho^2$; their pair distribution functions are $\bar{n}_2^0(\mathbf{r}; \rho_1)$ and $\bar{n}_2^0(\mathbf{r}; \rho_2)$, and their densities ρ_1 and ρ_2 , respectively. This is consistent with the interpretation of a straight portion of the graph $a(\rho, 0+)$ as a first-order transition.

In interpreting the results (9) and (14) it should be remembered that their derivation involves the limit process $\gamma \rightarrow 0$; they therefore yield information only about values of r small compared with the range γ^{-1} of the Kac potential. For example, (14) implies a two-phase structure on a length scale $\ll \gamma^{-1}$ but not necessarily on a scale $\gg \gamma^{-1}$.

VIII. SIMPLE UPPER BOUND ON $a(\rho, \gamma)$

Of the various upper and lower bounds on $a(\rho, \gamma)$ obtained in Sec. II to V, the only one simple enough to be useful for finite values of γ is the lower bound (3.12) for nonnegative-definite Kac potentials. The other bounds are too unwieldy because they involve the network of cells $\omega_1 \cdots \omega_M$.

A simple upper bound on $a(\rho, \gamma)$ can be obtained by a method due in essence to Gibbs.²⁴ We rewrite (1.11) in the form

$$Z(N, \Omega, \gamma) = Z^0(N, \Omega) \langle e^{-\beta W} \rangle^0 \quad (8.1)$$

where W is the long-range contribution to the potential energy and $\langle \rangle^0$ indicates a canonical average over the reference system. Since $e^{-\beta W}$ is convex we have by (1.6) and (7.1)

$$\begin{aligned} \langle e^{-\beta W} \rangle^0 &\geq \exp \langle -\beta W \rangle^0 \\ &= \exp \left[-\frac{1}{2}\beta \iint \gamma \phi(\gamma \mathbf{r}) \bar{n}_2^0(\mathbf{x}, \mathbf{x} + \mathbf{r}) d\mathbf{x} d\mathbf{r} \right]. \end{aligned} \quad (8.2)$$

Combining (1) and (2) and then taking the thermodynamic limit, we obtain

$$a(\rho, \gamma) \leq a^0(\rho) + \frac{1}{2}\gamma \int \phi(\gamma \mathbf{r}) \bar{n}_2^0(\mathbf{r}; \rho) d\mathbf{r} \quad (8.3)$$

where $\bar{n}_2^0$ is defined as in Sec. VII. This inequality may be strengthened in the manner used in going from (2.24) to (2.25), to give

$$a(\rho, \gamma) \leq \text{CE} \left\{ a^0(\rho) + \frac{1}{2}\gamma \int \phi(\gamma \mathbf{r}) \bar{n}_2^0(\mathbf{r}; \rho) d\mathbf{r} \right\}. \quad (8.4)$$

A system for which the right side of (8.4) can be evaluated is the one-dimensional system considered by Kac, Uhlenbeck, and Hemmer.⁶ In our notation it is defined by (1.4) and (1.5). For this system, the last term in (8.3) is essentially the Laplace transform of $\bar{n}_2^0$, and (8.4) becomes

$$\begin{aligned} a(\rho, \gamma) &\leq \text{CE} \{ a^0(\rho) \\ &+ \frac{1}{2}\alpha\gamma[(1 + \gamma\rho^{-1} - \gamma r_0)e^{\gamma r_0} - 1]^{-1} \} \end{aligned} \quad (8.5)$$

with

$$\begin{aligned} a^0(\rho) &= \rho kT \{ \log [\rho(1 - \rho r_0)^{-1} (2\pi\hbar^2/mkT)^{\frac{1}{2}}] - 1 \}. \end{aligned} \quad (8.6)$$

In the van der Waals limit (5) reduces to (2.25).

The argument which led to (4) also applies to lattice gases. For example, if the short-range potential is taken as

$$q(\mathbf{r}) = \begin{cases} +\infty & \text{if } \mathbf{r} = 0, \\ 0 & \text{if } \mathbf{r} \neq 0, \end{cases} \quad (8.7)$$

the part of the interaction potential which prevents more than one particle occupying any site, then $\bar{n}_2^0(\mathbf{r}; \rho)$ vanishes for $\mathbf{r} = 0$ and takes the value ρ^2 for $\mathbf{r} \neq 0$; consequently the lattice-gas analog of (4) leads to

$$a(\rho, \gamma) \leq \text{CE} \{ a^0(\rho) + \frac{1}{2}\gamma^2 \sum' w(\mathbf{r}, \gamma) \} \quad (8.8)$$

with

$$a^0(\rho) = kT[\rho \ln \rho + (1 - \rho) \ln (1 - \rho)]. \quad (8.9)$$

The sum $\sum'$ goes over the infinite lattice excluding $\mathbf{r} = 0$.

IX. DISCUSSION

We have shown that for a class of Kac potentials, including nonnegative-definite and nonpositive potentials, the thermodynamic free-energy density is given in the van der Waals limit by

$$a(\rho, 0+) = \text{CE} \{ a^0(\rho) + \frac{1}{2}\alpha\rho^2 \} \quad (9.1)$$

and the equation of state by Maxwell's modification of the corresponding van der Waals equation of state. If $\alpha < 0$, the graph of $a(\rho, 0+)$ may have straight portions; these correspond to first-order phase transitions both in the thermodynamic prop-

²³ J. E. Mayer, J. Chem. Phys. 15, 187 (1947); G. E. Uhlenbeck, P. Hemmer, and M. Kac, J. Math. Phys. 4, 229 (1963).

²⁴ See M. Girardeau, J. Chem. Phys. 40, 899 (1964).

erties and in the behavior of the pair distribution function for $r \ll \gamma^{-1}$. If $\alpha > 0$ on the other hand, the graph of $a(\rho, 0+)$ cannot have a straight portion and thermodynamically the system can have no phase transition. A paradoxical situation arises if the reference system has a phase transition and $\alpha > 0$; then by (7.9) the pair distribution function has the form characterizing a phase transition, yet there is no phase transition in the thermodynamic sense. The explanation is that the result (7.9), which indicates the coexistence of two phases, was obtained using the limit process $\gamma \rightarrow 0$ and may therefore be relied on only when $r \ll \gamma^{-1}$. On the other hand, the term $\frac{1}{2}\alpha\rho^2$ in $a(\rho, 0+)$ indicates that on the length scale where the Kac potential operates (distances $\approx$ or $\gg \gamma^{-1}$) the system is uniform since there is no transition. It appears therefore, that the repulsive Kac potential causes the distinct liquid and gas phases of a normal first-order transition to break into droplets or froth whose characteristic length is $\gg r_0$ but $\ll \gamma^{-1}$. This fact might possibly find a practical application.

Some of the results on which this paper is based can be generalized to quantum mechanics. The results of Sec. III generalize immediately to quantum mechanics, and so do those of Sec. II provided the boundary condition on the wavefunction is that it must vanish when the center of any particle touches the wall of the container. The main result of Sec. VIII also generalizes to quantum mechanics by virtue of Bogolyubov's inequality.²⁵ On the other hand Sec. IV and V do not generalize so readily. Unfortunately this means that we can at present evaluate $a(\rho, 0+)$ rigorously only for nonnegative-definite Kac potentials, which cannot produce a phase transition. Thus it remains to be shown that a van der Waals phase transition can occur in a quantum system.

The results of this paper can easily be generalized

to classical lattice gases. The proofs require only minor modifications, and the main results (5.31) and (5.32) are the same. Our results apply also to Ising spin systems since these are isomorphic to lattice gases. In this way the Bragg-Williams and Weiss theories can also be dealt with in a rigorous fashion.²⁶

Another direction in which our results might be generalized is to weaken the conditions (1.20) and (1.21). For example, for nonnegative-definite Kac potentials the hard-core condition (1.20a) can be replaced by the condition $q(r) > \text{const } r^{-\nu'}$ for small r , which is sufficient^{7,9} to ensure the existence of $a^0(\rho)$ and $a(\rho, \gamma)$. For more general Kac potentials the hard-core condition plays no part in the upper bound on $a(\rho, 0+)$ but is used to restrict the number of particles in a cell when lower bound on $a(\rho, 0+)$ is obtained. Possibly a more refined argument could dispense with the hard-core condition altogether.

A more interesting extension of this work would be to study Kac potentials satisfying neither of the conditions (i) and (ii) given at the end of Sec. V. For these potentials upper and lower bounds on $a(\rho, 0+)$ do not coincide, and it is possible that the behavior of the system is more complicated than in the van der Waals theory. For example the Kac potential might bring about spatial ordering with a length scale γ^{-1} . Finally from the physical point of view the most important extension of this work is to study the properties of the system when γ is finite but small. This is now being carried out along several lines.²⁷

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²⁵ Cited in Ref. 4 of V. V. Tolmachev, Dokl. Akad. Nauk SSSR 134, 1324 (1960) [Engl. transl.: Soviet Phys.-Doklady 5, 984 (1961)]. See also M. Girardeau, J. Chem. Phys. 41, 2945 (1964).

²⁶ In this connection see also the work of R. Brout, Phys. Rev. 115, 824 (1959) (and later publications) who considered expansions in the inverse number of interacting spins, and G. A. Baker, Phys. Rev. 126, 2072 (1962) who first considered the limiting process $\gamma \rightarrow 0$ in his study of spin systems.

²⁷ J. L. Lebowitz, G. Stell, and S. Baer, J. Math. Phys. 6, 1282 (1965).